

Complexometric titration

Presented By;-

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Specialization:- Pharmaceutical Chemistry

Complexometric Titration

Definition:- Complexometric titration is a type of volumetric analysis in which a **complexing agent (ligand)** is used to form a **stable, water-soluble complex** with the metal ion in solution. It is most commonly used for the determination of metal ions such as Ca^{2+} , Mg^{2+} , Zn^{2+} , etc.

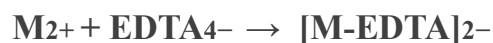
Key Features:

- It uses a **chelating agent** (most commonly EDTA).
- The endpoint is usually detected using a **metal ion indicator** (e.g., Eriochrome Black T).
- The titration involves **formation of a colored complex** which changes at the endpoint.

Example of Complexometric Titration

Example: Estimation of Calcium and Magnesium in Hard Water

Reaction:



Where $M^{2+} = Ca^{2+}$ or Mg^{2+}

Titrant: EDTA (Ethylenediaminetetraacetic acid)

Indicator: Eriochrome Black T (EBT)

Medium: Ammonia buffer (pH ~10)

Procedure (Simplified):

1. A sample of hard water is taken.
2. A few **drops** of Eriochrome Black T indicator are added – the solution turns **wine red** (metal-indicator complex).
3. The solution is titrated with standard EDTA solution.
4. Endpoint: Wine red color changes to **blue**, indicating that all Ca^{2+} and Mg^{2+} have reacted with EDTA.

Applications:

1. Water hardness analysis
2. Determination of metal ions in pharmaceuticals and food

Classification of Complexometric Titration

- 1. DIRECT TITRATION**
- 2. INDIRECT TITRATION**
- 3. BACK TITRATION**
- 4. REPLACEMENT OR SUBSTITUTION TITRATION**

1. Direct Titration

Direct Titration:-

- ❑ This is the simplest method, involving the direct titration of the metal ion solution with a standard EDTA solution until the endpoint is reached.
- ❑ It is suitable when the metal ion reacts rapidly and effectively with the indicator and EDTA at the appropriate pH.
- ❑ **Examples** of metals determined by direct titration include copper, zinc, barium, mercury, aluminium, lead, bismuth, and chromium.

2. Indirect Titration

Indirect or Alkalimetric Titration:

- ❑ Used for determining anions that do not directly react with EDTA.
- ❑ The anion is first precipitated by adding an excess of a metal cation.
- ❑ The excess metal ions in the filtrate are then titrated with a standard EDTA solution.
- ❑ This allows for the indirect estimation of the anion concentration.
- ❑ In alkalimetric titration, the reaction of the metal ion with disodium EDTA liberates hydrogen ions, which can then be titrated with a standard base like sodium hydroxide using an acid-base indicator.

3. Back Titration

Back Titration:

- ❑ In cases where the metal ion reacts too slowly with EDTA, precipitates at the required pH, or lacks a suitable indicator, an excess of standard EDTA solution is added to the metal ion solution.
- ❑ The excess unreacted EDTA is then back-titrated with a standard solution of another metal ion (e.g., zinc or magnesium).
- ❑ The difference between the initial EDTA added and the amount back-titrated gives the amount of EDTA that reacted with the metal ion of interest.

4. Replacement or Substitution Titration

Replacement or Substitution Titration:

- ❑ This method is employed when the direct or back titration methods fail to provide sharp endpoints due to the instability of the metal-indicator complex or a slow reaction with the indicator.
- ❑ An excess of a weak EDTA complex of another metal (e.g., Mg-EDTA or Zn-EDTA) is added to the analyte solution.
- ❑ The metal ion of interest displaces the metal from the weak EDTA complex, forming a more stable complex with EDTA.
- ❑ The liberated metal ions from the original weak complex are then titrated with a standard EDTA solution.

Metal Ions Indicators

Metal ion indicators are organic compounds used in **complexometric titrations**, especially with **EDTA**, to visually signal the **presence or absence of free metal ions** in a solution.

These indicators form **weak, colored complexes** with metal ions and change color when the metal ion is removed by a stronger chelating agent like EDTA.

Common Metal Ions Indicators

Indicator	Metal Ions Detected	Color Change at Endpoint
Eriochrome Black T	Ca^{2+} , Mg^{2+}	Wine-red $\rightarrow$ Blue
Murexide	Ca^{2+}	Pink $\rightarrow$ Purple
Calcon	Ca^{2+} , Mg^{2+}	Red $\rightarrow$ Blue
Xylenol Orange	Fe^{3+} , Bi^{3+}	Red $\rightarrow$ Yellow
PAN (1-(2-pyridylazo)-2-naphthol)	Many metal ions	Red $\rightarrow$ Yellow/orange

Masking Reagents

Definition:- Masking agents are **chemical substances** that **prevent certain metal ions** from reacting with the titrant (e.g., EDTA) by **forming stable, non-reactive complexes**. This allows selective titration of desired metal ions in the presence of others.

Purpose of Masking:

- ☐ To **eliminate interference** from unwanted metal ions.
- ☐ To **enhance selectivity** in complexometric titrations.

Examples of Masking Agents

Masking Agent	Masked Metal Ion	Remarks
Potassium cyanide (KCN)	Cu^{2+} , Cd^{2+} , Zn^{2+}	Forms stable cyanide complexes
Thioglycolic acid	Hg^{2+} , Pb^{2+}	Forms stable complexes with heavy metals
Triethanolamine (TEA)	Al^{3+} , Fe^{3+} , Cr^{3+}	Used to mask trivalent metal ions
Oxalate or tartrate	Fe^{3+} , Al^{3+} , Mn^{2+}	Binds strongly to metals in alkaline conditions
EDTA (in excess)	Ca^{2+} , Mg^{2+}	Can itself act as a masking agent if added earlier

Demasking Reagents

Definition:-Demasking agents are chemicals that **release a masked metal ion** by breaking the masked complex, making the metal ion **available for titration**.

Purpose of Demasking:

- ☐ To **selectively titrate** masked metal ions **after** the titration of other ions.
- ☐ Allows **stepwise analysis** of multiple metal ions.

Examples of Demasking Agents:

Demasking Agent	Releases Metal From	Remarks
Formaldehyde	CN ⁻ complexes (e.g., Cu ²⁺ -CN ⁻)	Destroys cyanide complexes
H ₂ S (hydrogen sulfide)	Cu ²⁺ , Pb ²⁺	Precipitates metal sulfides
Acetone or acids	Oxalate, tartrate complexes	Breaks weak complexes
UV light (photolysis)	Some masking complexes	Photochemically decomposes masking agent



Estimation Of Magnesium Sulphate

Link:- <https://pharmrecord.com/bp108p/>

Estimation Of Calcium Gluconate

Link:- <https://pharmrecord.com/bp108p/>



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